Electron-Phonon Coupling and CT-Character in the lowest Triplet Excited State of Anthracene EDA-Complex Crystals

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Photoexcitation spectra of triplet ($T_1 \leftarrow S_0$) zero-phonon lines and phonon sidebands in different anthracene electron donor-acceptor (EDA) complex crystals (A-PMDA, A-TCNB, A-TCPA) have been analyzed between 1.3 K and 50 K at high spectral resolution. From the electron-phonon coupling strength at T = 0 K values of the charge-transfer (CT) character in the range between 6% and 10% are calculated. The differences in these values are found to be correlated with the energetic positions of the triplet state, which are explained within the framework of the Mulliken theory.

1. Introduction

In this work various organic EDA-complex crystals have been investigated which are built up in alternating stacks of the donor anthracene and the respective acceptor molecule (PMDA = pyromellitic-acid-dianhydride, TCNB = tetracyanobenzene, TCPA = tetrachlorphthalic anhydride) [1–4].

The electronic states of such complexes commonly are described by the Mulliken valence-bond theory [5]. The wave functions read as

$$\Psi_{\mathrm{CT}} = c_1\, \Psi_{\mathrm{AD}} + c_2\, \Psi_{\mathrm{A-D+}}\,. \tag{1}$$

They are constructed as a superposition of the no-bond wave function Ψ_{AD} and the completely ionic wave function $\Psi_{\mathrm{A-D+}} \cdot c_2$ is a measure for the degree of the charge-transfer.

The complex crystals A-PMDA, A-TCNB and A-TCPA belong to the class of weak charge transfer crystals, where in the ground state $c_1 \gg c_2$. From the optical spectra $c_1 < c_2$ is concluded for the singlet excited state S_1 [6], but ESR data show $c_2 \gg c_2$ for the triplet excited state T_1 [7–10].

The former conclusion is based on theoretical predictions about an interrelationship between charge-transfer character and electron-phonon coupling (EPC) strength (see e.g. [11]). It is consistent on the other hand with the fact that in the triplet optical spectra weak EPC allows the observation of sharp zero-phonon lines clearly distinguished from phonon sidebands.

A common feature of the phosphorescence spectra of various EDA systems is a shift of the energy of the $T_1 \leftarrow S_0$ transition relative to that in the crystal of the donor molecule. Blue-shifts ranging up to 500 cm^{-1} are reported for the anthracene donor systems A-TNB (trinitrobenzene) [12], A-PMDA [13] and A-TCNB [8, 14], whereas a red-shift of 263 cm^{-1} is observed for pyrene-PMDA [15]. However, in these cases the phosphorescence actually originated from (x) trap states, providing only a rough measure for the excitonic 0.0 energy.

The aim of the present work was twofold: First, to determine the charge-transfer character of the different systems explicitely from the optical Debye-Waller factor obtained from high resolution excitation spectra. Second, to compare the energetic positions of the excitonic $T_1 \leftarrow S_0$ transitions and to find a possible correlation between CT-character and line-shifts.

2. Experimental

Anthracene was vacuum-sublimed and zone-refined by standard techniques. Commercially available PMDA and TCPA were zone-refined, whereas TCNB was synthesized and purified by W. Tuffentsammer. Single crystals of the complexes could be grown from solutions of equimolar (1:1) mixtures of donor and acceptor material.

Photoexcitation spectroscopy with a tunable cw ring dye laser (dye: DCM) has been applied in the temperature range between 1.3 K and 50 K. In broad and narrow band version the spectral resolution was 0.5 cm^{-1} and 0.0005 cm^{-1}, respectively.

The triplet absorption was monitored via delayed fluorescence or phosphorescence in the limit of linear dependence on the excitation intensity. The observed spectra are identical for both modes of detection.

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3. Experimental results

Temperature dependent triplet excitation spectra of the three anthracene complex crystals were measured (A-TCNB is shown as an example in Fig. 1) and analyzed with respect to the positions of the zero phonon lines and the relative intensities of the phonon sidebands. From the fact that the vibronic progressions coincide with those found in anthracene it is concluded that the investigated triplet exciton states are localized at the donor molecules. This work concentrates on the spectral region of the purely electronic 0.0 transition. In the case of A-TCPA two 0.0 lines separated by 40 cm^{-1} are found exhibiting the same spectroscopic behavior. Since both zero-phonon lines are accompanied by ^{13}C-isotopic satellites and phonon sidebands, they are attributed to two different triplet exciton bands corresponding to the two inequivalent stacks [4] in the A-TCPA crystal.

Zero-phonon line positions:

The experiments reveal a general blue-shift of the triplet exciton state in the different systems. In Fig. 2 the measured zero-phonon line positions are given in comparison with the energetic position of the center of gravity of the exciton band in the anthracene crystal [16].

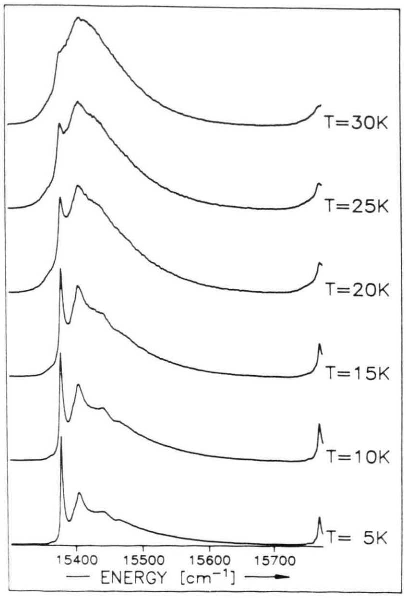

Fig. 1. Temperature dependent excitation spectra of the triplet T_1 0.0 region of A-TCNB.

The following contributions to the lineshifts are possible:

- different complex binding energies depending on the specific acceptor molecule,
- different solvent shifts of the complexes in the crystal,
- Mulliken theory [5] predicts a shift of the singlet and triplet states.

The first and second contribution have been ruled out as the predominant ones in additional experiments. First, similar experiments were performed on complex crystals with naphthalene as donor and the same acceptor molecules [17]. In these experiments no equivalent sequence for the lineshifts is found.

Second, the order of magnitude of solvent shift contributions can be obtained from experiments on mixed crystals. Our measurements on A-TCNB in N-TCNB (10^{-4} mole/mole) yielded a matrix-induced change of about $+18$ cm^{-1} [17], whereas the literature value for A-PMDA in N-PMDA is -65 cm^{-1} [18]. These values are small as compared with the shifts observed in the anthracene crystals. The actual explanation of the lineshift will be given in the discussion.

^{13}C satellite lines:

Using narrow band excitation additional satellites of the zero-phonon lines displaced to higher energies are detected in all three systems. Because of their energetic shift between 1.1 cm^{-1} and 3.0 cm^{-1} and their relative intensities of 4% and 2%, resp., they are at-

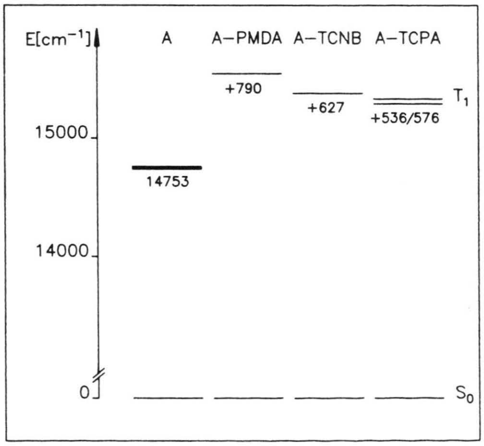

Fig. 2. Triplet zero-phonon line positions of A-PMDA, A-TCNB, A-TCPA and uncomplexed anthracene ($T = 5$ K).

tributed to naturally abundant ^{13}C-mono-substituted isotopic anthracene impurities, in analogy to the case of uncomplexed anthracene crystals [16]. From the fact that the isotopic shifts are not measurably changed (within 0.1 cm^{-1}) by quasiresonance effects as compared to anthracene, an upper limit of 1 cm^{-1} for the triplet exciton bandwidth of the three anthracene complex crystals can be deduced.

Phonon sidebands:

In Fig. 3 the phonon sidebands accompanying the zero-phonon lines are shown for the complex crystals in comparison with the anthracene crystal at helium temperature. The spectra are normalized to the intensity of the sideband maxima.

In contrast to anthracene [16] the phonon sidebands of the complex crystals do not depend on the polarisation of the excitation light and do not reflect the Raman frequencies. The overall shape of the phonon sidebands of the complex crystals is similar and the energetic position of the main sideband maximum is about 26 cm^{-1} with respect to the zero-phonon lines.

From the relative intensities of zero-phonon lines I_{ZPL} and phonon sidebands I_{Ph} the optical Debye-Waller factor $S = -\ln(I_{\text{ZPL}}/I_{\text{ZPL}} + I_{\text{Ph}})$ as a measure for the EPC strength was determined. For the different complex crystals different values of S were obtained, which strongly increase with temperature. In contrast, for anthracene the value of S is smaller ($S = 0.2$) [16] and does not depend on temperature. These results are in agreement with the fact that the triplet excitation is more localized in the complex crystals. In the case of localized EPC the temperature dependence of S can be described by

$$S(T) = S(0) \cdot \left(1 + \frac{2\pi^2}{3} \frac{T^2}{T_{\text{D}}^2}\right). \tag{2}$$

The experimental values $S(T)$ in Fig. 4 were fitted according to this formula. The best fits for all three complex crystals use the same value for the Debye temperature, $T_{\text{D}} = 66$ K.

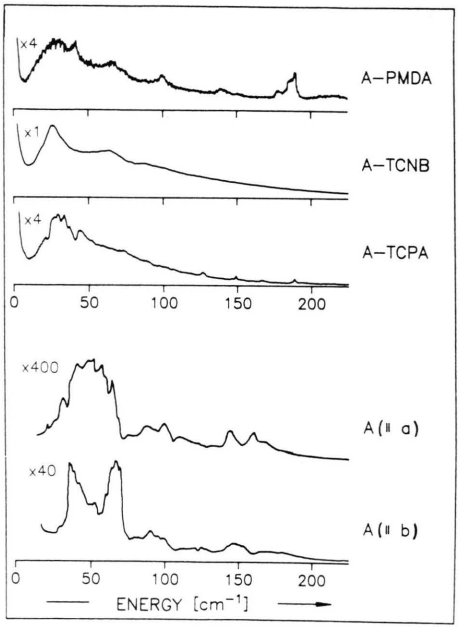

Fig. 3. Unpolarized phonon sidebands of the triplet 0.0 transition in A-PMDA, A-TCNB, A-TCPA in comparison with the strongly polarized phonon sidebands of anthracene.

4. Discussion

Correlation between EPC and CT-character:

Theoretical considerations of the electron-phonon interaction in donor-acceptor crystals [11] predict a correlation between the EPC strength S and the relative charge transfer q, respective CT-character q^2, in the excited state, $S \sim q^4$. Assuming that the phonon sidebands can be characterized by a single phonon frequency ω_{n}, according to [19] the functional dependence of S reads as

$$S = \frac{q^4}{\varepsilon^2\, \omega_{\text{n}}^3\, d^4\, \hbar\, m} \cdot \left(\frac{7}{32\pi}\right)^2, \tag{3}$$

where d is the intermolecular distance within the complex (derived from crystal structure) and m is the mass of the acceptor molecule.

In first approxiamtion a value of $\omega_{\text{n}} = 4.7 \cdot 10^{12}$ sec^{-1} is used, which corresponds to the maximum position (26 cm^{-1}) of the phonon sidebands (see Section 3).

S in (2) defines the coupling strength in the limit $T = 0$ K, which can be deduced from an extrapolation of the temperature dependencies in Figure 4. These values $S(0)$ are listed in Table 1 together with the calculated CT-character q^2 using $\varepsilon = 2.5$ [20]. An accuracy of ± 10% in the calculation of $S(0)$ and the determination of the single dominating phonon frequency ω_{n} allow a precision of ± 20% for the calculated CT-characters. This does not include the limitations of the

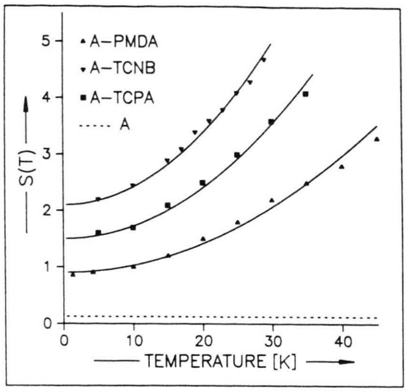

Fig. 4. Electron-phonon coupling strength S as a function of temperature for A-PMDA, A-TCNB, A-TCPA; experimental values and theoretical curves, see text.

simplifying model of a single dominating ω_n, which influence, however, the values for the three systems equally. In the literature different values for the CT-character from magnetic resonance measurements are reported (from D and E values obtained in ESR and ODMR or from hyperfine splittings observed in ESR):

A-PMDA: 5% [9] from ESR,
A-TCNB: 3%, 5% [8, 7] from hfs;
2.5%, 5% [14, 10] from D, E,
A-TCBA: 3% ... 4% [21] from D, E.

These values do not provide a similar sequence for the three systems, what could be due to the different types of measurement.

Lineshifts according to Mulliken theory:

Using the ansatz (1) for the wavefunction of EDA complexes, perturbation theory can be applied to calculate energetic positions of the singlet and triplet states [9]. The perturbed levels are shifted to lower energy relative to the corresponding uncomplexed donor state by ΔS_0 and ΔT_0, respectively:

$$\begin{aligned} \Delta S_0 &= \frac{({}^1\mathrm{H}_{01} - \mathrm{S}_{01}\,{}^1\mathrm{W}_0)^2}{{}^1\mathrm{W}_1 - {}^1\mathrm{W}_0} = \frac{V_1^2}{{}^1\mathrm{W}_1 - {}^1\mathrm{W}_0}, \\ \Delta T_0 &= \frac{({}^3\mathrm{H}_{01} - \mathrm{T}_{01}\,{}^3\mathrm{W}_0)^2}{{}^3\mathrm{W}_1 - {}^3\mathrm{W}_0} = \frac{V_3^2}{{}^3\mathrm{W}_1 - {}^3\mathrm{W}_0} \end{aligned} \tag{4}$$

with

${}^1\mathrm{W}_0$, ${}^3\mathrm{W}_0$, ${}^1\mathrm{W}_1$, ${}^3\mathrm{W}_1$
= singlet/triplet ground/excited states,
$\mathrm{H}_{01} = \langle \Psi_0 | \mathrm{H} | \Psi_1 \rangle$,
$S_{01} = \langle \Psi_0 | \Psi_1 \rangle$.

Table 1.

Crystal	$S(T = 0\ \mathrm{K})$	q/e	CT-character q^2/e^2
A-PMDA	0.9	0.26	6.7%
A-TCNB	2.1	0.31	9.6%
A-TCPA	1.4	0.28	8.0%

As a result, the transition $E(3\mathrm{L}^*)$ between the ground state and the local triplet excited state in the complex is displaced with respect to the corresponding transition $E(3\mathrm{L})$ in the donor crystal ($E(3\mathrm{L}^*)$ and $E(3\mathrm{L})$ according to [9])

$$E(3\mathrm{L}^*) = E(3\mathrm{L}) + \Delta S_0 - \Delta T_0 \,. \tag{5}$$

Perturbation theory further provides a relationship between the CT-character q^2 of the localized triplet state of the complex and the parameters of the expressions (4):

$$\frac{q}{e} = \frac{V_3}{{}^3\mathrm{W}_1 - {}^3\mathrm{W}_0} \,. \tag{6}$$

Consequently (4–6) predict a correlation between the energetic position of the complex excited state and its CT-character. Normalizing the energy of the singlet ground state, ${}^1\mathrm{W}_0 = 0$, the transition energies $E(3\mathrm{L}^*)$ are given by

$$E(3\mathrm{L}^*) - E(3\mathrm{L}) = \frac{V_1^2}{{}^1\mathrm{W}_1} - V_3\, q/e \,. \tag{7}$$

Equation (7) equally holds for the three anthracene complex crystals. It can be used to explain the sequence of the energy displacements in Fig. 2, taking into account the q values determined in Section 4.1. The values for ${}^1\mathrm{W}_1$ are taken from the energetic positions of the singlet charge transfer states observed in the optical spectra (A-PMDA: 17 900 cm^{-1}, A-TCNB: 19 000 cm^{-1}, A-TCPA: 20 400 cm^{-1}). Inserting the experimental data for the different systems, (7) can be fulfilled as expected with the same parameter values $V_1 = 4\,810$ cm^{-1} and $V_3 = 1\,930$ cm^{-1} for all systems.

5. Conclusion

In this paper three anthracene complex crystals were investigated and evidence is given for the correlation ($S \sim q^4$) between EPC strength and CT-character. Thus the optical method provides a sensitive spectroscopic probe for the charge transfer in the excited triplet state. In addition it is shown that experimentally observed distinct blue-shifts can be explained using perturbation theory.

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